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## (54) VALVE SEAT MADE OF Fe-BASE SINTERED ALLOY EXCELLENT IN WEAR RESISTANCE

(57) A valve seat made of Fe-based sintered alloy, the Fe-based sintered alloy comprising, as a whole composition, by weight C: 0.5 - 2 %, Si: 0.05 - 1 % Si, Co: 8 - 16 %, Cr: 2 - 8 %, Mo: 1.5 - 6 %, W: 1.5 - 6 %, Ni: 0.5 - 2 %, Nb: 0.05 - 1 %, and calcium fluoride: 1 - 15 %, with a balance of Fe and inevitable impurities, wherein the Fe-based sintered alloy has such a structure that Co-based alloy hard particles A, which comprise Co-Mo-Cr alloy and have high temperature wear resistance, and Cr-based alloy hard particles B, which comprise Cr-W-Co-Fe alloy and have ordinary temperature wear resistance, are dispersed and distributed in an alloy steel base at a ratio of 6 - 26 area % in a total amount and further CaF<sub>2</sub> are dispersed and distributed in the alloy steel base at a ratio of 3 - 45 area ratio likewise, and the Fe-based sintered alloy has a porosity of 5 - 25 %. Further, copper or copper alloy, or lead or lead alloy is infiltrated into the Fe-based sintered alloy, when necessary. With this structure, there can be provided a valve seat excellent in wear resistance made of the Fe-based sintered alloy.

**Description****Technical Field**

5 [0001] The present invention relates to a valve seat made of Fe-based sintered alloy, as a structural member for internal combustion engines such as diesel engines, gasoline engines and so forth.

**Background Art**

10 [0002] As disclosed in, for example, Japanese Unexamined Patent Publication No. 55-164063, Japanese Unexamined Patent Publication No. 58-178073 and the like, there have been proposed many valve seats which are made of hard-particle-dispersing type Fe-based sintered alloy as valve seats for internal combustion engines made of Fe-based sintered alloy.

15 [0003] In contrast, recently, the output of internal combustion engines and the size thereof have been greatly increased, by which valve seats, which are a structural member of the internal combustion engines, are compelled to operate in the environment of a higher temperature. However, when the conventional Fe-based sintered alloy valve seats and many other valve seats are used in the environment of a higher temperature, they are abruptly worn and the life thereof is ended in a relatively short period of time.

**DISCLOSURE OF THE INVENTION**

20 [0004] To cope with the above problem, the inventors conducted research to develop, from the above point of view, a valve seat which exhibited excellent wear resistance even if it was exposed to the environment of a high temperature and obtained the following result. As a result of the research, we have developed a valve made of Fe-based sintered 25 alloy which comprises, as a whole composition, (hereinafter, % as to composition is wt%)

C: 0. 5 - 2 %, Si: 0.05 - 1 %,  
 Co: 8 - 16 %, Cr: 2 - 8 %,  
 Mo: 1.5 - 6 %, W: 1.5 - 6 %,  
 30 Ni: 0.5 - 2 %, Nb: 0.05 - 1 %, and  
 calcium fluoride: 1 - 15 %,

35 with a balance of Fe and inevitable impurities. Further, the Fe-based sintered alloy has such a structure that Co-based hard particles A, which comprise Co-Mo-Cr alloy and have high temperature wear resistance, and Cr-based alloy hard particles B, which comprise Cr-W-Co-Fe alloy and have ordinary temperature wear resistance, are dispersed and distributed in an alloy steel base at a ratio of 6 - 26 area % in a total amount when they are observed on a structure photograph recorded by an optical microscope as well as the ratio of the hard particles A to the hard particles is 25 - 75 area % and further calcium fluoride particles are dispersed and distributed in the alloy steel base at a ratio of 3 - 45 area ratio likewise, and the Fe-based sintered alloy has a porosity of 5 - 25 %. As a result, in the valve seat made of the Fe-based sintered alloy, since the hard particles A are particularly excellent in high temperature wear resistance, excellent wear resistance can be secured even if the valve seat is used at a high temperature. In addition, excellent ordinary temperature wear resistance can be secured by the hard particles B and the wear resistance can be further more improved by the lubricating property improving effect achieved by the CaF<sub>2</sub> particles. Further, the wear resistance particularly at the initial operation of an internal combustion engine and when the internal combustion engine is in operation at a low speed can be improved by the cooperation of the lubricating property improving effect and the ordinary temperature wear resistance improving effect. As a result, the valve seat exhibits excellent wear resistance as a whole for a long time. Further, the thermal conductivity and the strength of the Fe-based sintered alloy can be improved by the infiltration of the copper or the copper alloy, whereas, the lubricating property, vibration restricting property and property to cut off the Fe-based sintered alloy can be improved by the infiltration of the lead or the lead alloy.

50 [0005] The present invention, which has been achieved based on the result of the above research, is characterized in a valve seat excellent in wear resistance made of Fe-based sintered alloy, the Fe-based sintered alloy comprises, as a whole composition, by weight

C: 0. 5 - 2 %, Si: 0.05 - 1 %,  
 Co: 8 - 16 %, Cr: 2 - 8 %,  
 Mo: 1.5 - 6 %, W: 1.5 - 6 %,  
 55 Ni: 0.5 - 2 %, Nb: 0.05 - 1 %, and  
 calcium fluoride: 1 - 15 %,

with a balance of Fe and inevitable impurities, wherein the Fe-based sintered alloy has such a structure that Co-based alloy hard particles A, which comprise Co-Mo-Cr alloy and have high temperature wear resistance, and Cr-based alloy hard particles B, which comprise Cr-W-Co-Fe alloy and have ordinary temperature wear resistance, are dispersed and distributed in an alloy steel base at a ratio of 6 - 26 area % in a total amount when they are observed on a structure photograph recorded by an optical microscope as well as the ratio of the hard particles A to the hard particles is 25 - 75 area % and further calcium fluoride particles are dispersed and distributed in the alloy steel base at a ratio of 3 - 45 area ratio likewise, and the Fe-based sintered alloy has a porosity of 5 - 25 %, and copper or copper alloy, or lead or lead alloy is infiltrated into the Fe-based sintered alloy, when necessary.

[0006] The valve seat of the present invention uses alloy steel powder serving as base forming alloy powder which includes 0.2 - 3 % C, 0.5 - 7 % Ni, 1 - 12 % Co, 0.05 - 1.5 % Nb, and further includes, when necessary, one kind or two or more kinds of 0.3 - 6 % Cr, 0.2 - 6 % Mo, 0.5 - 6 % W and 0.1 - 1 % Si, with a balance Fe and inevitable impurities; Co-based alloy powder serving as hard particles A forming alloy powder which comprises Co-Mo-Cr alloy including 20 - 35 % Mo, 5 - 10 % Cr and 1 - 4 % Si, with a balance Co and inevitable impurities; and Cr-based alloy powder serving as hard particles B forming alloy powder which comprises Cr-W-Co-Fe alloy including 0.5 - 3 % C, 15 - 30 W, 15 - 30 % Co, 5 - 15 % Fe, 0.2 - 2 % Nb and 0.2 - 2 % Si, with a balance of Cr and inevitable impurities. These powder materials are blended with each other at a prescribed ratio together with CaF<sub>2</sub> powder which is also prepared as a powder material likewise. They are mixed under ordinary conditions and formed to a prescribed shape with a press and sintered. Further, copper or copper alloy, or lead or lead alloy is infiltrated into them, when necessary. The valve seat of the present invention is made by the above processes.

[0007] As to the base forming powder material, element powders, or element powders and alloy powders may be used in place of the alloy steel powder by blending them so that they have the same composition as that of the alloy steel powder.

[0008] Next, in the valve seat of the present invention, the reasons why the whole composition of the Fe-based sintered alloy constituting the valve seat, the ratio of the hard particles and the CaF<sub>2</sub> particles and further the porosity are defined as described above will be described.

#### (A) Composition

##### (a) C

[0009] A component C has an action for strengthen the base metal by being dissolved in the base metal in a solid state, for improving the wear resistance of the base metal by forming carbide which disperses in the base metal and for improving the wear resistance of the hard particles A and B by being contained in any of them. However, the C content in an amount not larger than 0.5 % could not obtain a desired improving effect from the action, whereas the C content exceeding 2 % would abruptly increase a counterpart attracting property. Therefore, the C content is defined to 0.5 - 2 %, and preferably to 0.8 - 1.5 %.

##### (b) Si

[0010] A component Si has an action for forming hard intermetallic compounds by being mainly contained in the hard particles A and B and contributing to the improvement of the wear resistance of them by it. However, the Si content in an amount not larger than 0.05 % could not obtain a desired improving effect from the action, whereas the Si content exceeding 1 % would embrittle the hard particles B themselves and deteriorate the wear resistance thereby. Therefore, the Si content is defined to 0.05 - 1 %, and preferably to 0.2 - 0.7 %.

##### (c) Co

[0011] A component Co has an action for strengthening the base metal by being dissolved in it in a solid state as well as contributing to the improvement of the high temperature wear resistance of the hard particles A, and for strengthening the hard particles B by being dissolved in it in a solid state. However, the Co content in an amount not larger than 8 % could not obtain a desired effect from the action, whereas the Co content exceeding 16 % would deteriorate the wear resistance of the valve seat itself. Therefore, the Co content is defined to 8 - 16 %, and preferably to 10 - 14 %.

##### (d) Cr

[0012] A component Cr has an action for strengthening the base metal by being dissolved in it in a solid state, for improving the ordinary temperature wear resistance of the hard particles B by forming carbide and intermetallic compounds in them by being mainly contained therein as a main component, and further for contributing to the improvement

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of the high temperature wear resistance of the hard particles A by forming carbide and intermetallic compounds in them likewise by coexisting therein with Co. However, the Cr content in an amount not larger than 2 % could not obtain a desired effect from the action, whereas, the Cr content exceeding 8 % would deteriorate a sintering property and could not secure a desired strength in the valve seat. Therefore, the Cr content is defined to 2 - 8 %, and preferably to 4 - 6 %.

5 (e) Mo

[0013] A component Mo has an action for strengthening the base metal by being dissolved in it in a solid state, and for improving the high temperature wear resistance of the hard particles A by being mainly contained in them without being substantially contained in the hard particles B through the coexistence of it with Co. However, the Mo content in an amount not larger than 1.5 % could not obtain a desired effect from the action, whereas, the Mo content exceeding 6 % would increase a counterpart attracting property. Therefore, the Mo content is defined to 1.5 - 6 %, and preferably to 2 - 4 %.

15 (f) W

[0014] A component W has an action for contributing to the improvement of the ordinary temperature wear resistance of the hard particles B by forming carbide and intermetallic compounds in them by being contained therein. However, the W content in an amount not larger than 1.5 % could not obtain a desired effect from the action, whereas, the W content exceeding 6 % would increase a counterpart attracting property. Therefore, the W content is defined to 1.5 - 6 %, and preferably to 2 - 4 %.

25 (g) Ni

[0015] A component Ni has an action for strengthening the hard particles A and B by being contained in any of them. However, the Ni content in an amount not larger than 0.5 % could not obtain a desired effect from the action, whereas, the Ni content exceeding 2 % would deteriorate the wear resistance. Therefore, the Ni content is defined to 0.5 - 2 %, and preferably to 0.8 - 1.5 %.

30 (h) Nb

[0016] A component Nb has an action for contributing to the improvement of the ordinary temperature wear resistance of the hard particles B by forming carbide in them by being mainly contained therein. However, the Nb content in an amount not larger than 0.05 % could not obtain a desired effect from the action, whereas, the Nb content exceeding 1 % would increase a counterpart attracting property. Therefore, the Nb content is defined to 0.05 - 1 %, and preferably to 0.2 - 0.7 %.

35 (i) CaF<sub>2</sub>

[0017] A component CaF<sub>2</sub> has an action for improving a lubricating property and improving the wear resistance by it, and in particular for improving the wear resistance at the initial operation of an internal combustion engine and when the internal combustion engine is in operation at a low speed through the coexistence of it with the hard particles B. However, when the CaF<sub>2</sub> content is in an amount not larger than 1 %, the ratio of CaF<sub>2</sub> which is dispersed and distributed in the base metal would be not larger than 3 area % and a desired effect could not be obtained from the action. Whereas, when the CaF<sub>2</sub> content is in an amount exceeding 15 %, the ratio of CaF<sub>2</sub> which is dispersed and distributed in the base metal would exceed 45 areas % which is excessively large and strength is lowered thereby. Therefore, the CaF<sub>2</sub> content is defined to 1 - 15 %, and preferably to 3 - 10 %.

40 (B) Ratio of hard particles

[0018] As described above, the valve seat is provided with the excellent high and ordinary temperature wear resistance by the respective hard particles A and B. Therefore, when the ratio of the hard particles A to the hard particles A and B is not larger than 25 area %, desired high temperature wear resistance could not be obtained. Whereas, when the ratio of the hard particles A exceeds 75 area %, desired ordinary temperature wear resistance could be secured as well as the wear resistance at the initial operation of an internal combustion engine and when the internal combustion engine is in operation at a low speed could not be secured through the coexistence of the hard particles B with the CaF<sub>2</sub> particles. This is because the ratio of the hard particles B is made relatively too small. Accordingly, the ratio of the hard particles A is determined to 25 - 75 area %, and preferably to 40 - 60 vol%.

[0019] When the whole ratio of the hard particles A and B is not larger than 6 area %, desired wear resistance could not be secured. Whereas, when the whole ratio of the hard particles A and B exceeds 26 area %, not only a counterpart attacking property would be abruptly increased but also strength would be lowered. Thus, the whole ratio is determined to 6 - 26 area %, and preferably to 10 - 20 area %.

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(C) Ratio of CaF<sub>2</sub>

[0020] As described above, CaF<sub>2</sub> particles have the action for improving the wear resistance by the lubricating property improving effect of them as well as for improving the wear resistance at the initial operation of an internal combustion engine and when the internal combustion engine is in operation at a low speed in cooperation with the ordinary temperature wear resistance improving effect of the hard particles B. However, when the ratio of the CaF<sub>2</sub> particles is not larger than 3 area %, a desired improving effect could not be obtained from the action, whereas, when the ratio of the CaF<sub>2</sub> particles exceeds 45 area %, strength would be lowered. Therefore, the ratio of the CaF<sub>2</sub> particles is determined to 3 - 45 area %, and preferably to 9 - 30 area %.

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## (D) Porosity

[0021] When a porosity is not larger than 5 %, a lubricating property improving effect resulting from an oil maintaining effect could not be expected. In addition, copper and copper alloy, or lead and lead alloy would be unevenly infiltrated and the effect of the infiltration of them could not be sufficiently exhibited. Whereas, when the porosity exceeds 25 %, the reduction of strength and wear resistance could not be avoided. Therefore, the porosity is determined to 5 - 25 %, and preferably to 10 - 20 %.

## 20 BEST MODE OF CARRYING OUT THE INVENTION

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[0022] The valve seat of the present invention will specifically be described with reference to an example.

[0023] First, base metal forming alloy powders M-1 to M-13, hard particles A forming alloy powders A-1 to A-6, and hard particles B forming alloy powders B-1 to B-13 each having the average particle size and the composition shown in Table 1 to Table 3 were prepared; they were blended with each other according to the combination shown in Table 4, they were further blended with CaF<sub>2</sub> powder, respectively which was prepared as material powder likewise and had a particle size of -200 mesh at a prescribed ratio; zinc stearate was added to the resultant powders in the amount of 1 % and they were mixed by a mixer for 30 minutes; thereafter, they were pressed to green compacts at a prescribed pressure within the range of 5 - 7 ton/cm<sup>2</sup>; then, the green compacts were held at 500°C for 30 minutes and degreased; and the green compacts were sintered under the conditions that they were held at a prescribed temperature within the range of 1180 - 1250°C for one hour in the atmosphere of a decomposed ammonia gas. With the above processes, the valve seats 1 - 13 of the present invention and comparative valve seats 1 - 4 were made, respectively. Each of the valve seats was composed of Fe-based sintered alloy which had the whole composition, the ratios of the hard particles and the CaF<sub>2</sub> particles (measured with an image analyzing apparatus based on structure photographs recorded by a  $\times 100$  optical microscope) and the porosity shown in Tables 5 - 8, respectively. Further, each of the valve seats had a dimension of outside diameter: 34 mm  $\times$  minimum inside diameter: 27 mm  $\times$  thickness: 7.2 mm.

[0024] The ratio of the hard particles and further the ratio of the CaF<sub>2</sub> particles in the comparative valve seats 1 - 4 fall outside the range of the present invention, and thus the whole composition of them falls outside the range of the composition of the present invention.

[0025] Further, the copper-infiltrated valve seats 1 - 13 of the present invention and comparative copper-infiltrated valve seats 1 - 4 were made, respectively in the following manner. That is, the valve seats 1 - 13 of the present invention and the comparative valve seats 1 - 4 were used as main bodies; an infiltrating material composed of pure copper, Cu - 3 % Co alloy (hereinafter, referred to as Cu alloy 1), Cu - 3 % Fe - 2 % Mn - 2 % Zn alloy (hereinafter, referred to as Cu alloy 2), or Cu - 30 % Zn alloy (hereinafter, referred to as Cu alloy 3) was placed on each of the main bodies in the combination shown in Table 9; and the main bodies were subjected to copper or copper alloy infiltrating processing in the above state under the conditions that they were held at 1100 °C for 15 minutes in the atmosphere of a methane denatured gas.

[0026] In the same way, the lead-infiltrated valve seats 1 - 13 of the present invention and comparative lead-infiltrated valve seats 1 - 4 were made, respectively in the following manner. That is, the valve seats 1 - 13 of the present invention and the comparative valve seats 1 - 4 were used as main bodies; an infiltrating material composed of pure lead, Pb - 4 % Sb alloy (hereinafter, referred to as alloy a), or Pb - 5 % Sn alloy (hereinafter, referred to as alloy b), was placed on each of the main bodies in the combination shown in Table 10; and the main bodies were subjected to lead or lead alloy infiltrating processing under the conditions that they were dipped into a bath in which the infiltrating material was heated in a nitrogen atmosphere with a pressure of 8 kg/cm<sup>2</sup> applied to the surface of the heated infiltrating material.

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[0027] Next, the wear test of the various types of the resultant valve seats was carried out using a table type valve seat wear tester under the following conditions, and the maximum worn depth of the valve sheets and the maximum worn depth of a valve as a counterpart were measured.

- 5      Valve material: SUH-3  
      Valve heating temperature: 800°C  
      Number of valve seating: 3000 times/min  
      Atmosphere: combustion gas composed of a propane gas having a pressure of 0.4 kg/cm<sup>2</sup> and an oxygen gas having a flow rate of 1.5 l/min  
10     Valve seat heating temperature (water cooled): 300 - 400°C  
      Seating load: 30 kg  
      Test time: 20 cycles each including continuous operation of one hour and interruption of 10 minutes Tables 7 - 10 show the results of the measurement.

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Table 1

| Type                                   | Average particle size ( $\mu\text{m}$ ) | Composition (wt %) |      |     |      |     |     |     |      | Fe + impurities |
|--|---|--------------------|------|-----|------|-----|-----|-----|------|-----------------|
|  |   | C                  | Co   | Ni  | Nb   | Cr  | Mo  | W   | Si   |                 |
| <u>base metal forming alloy powder</u> |   |                    |      |     |      |     |     |     |      |                 |
| M-1                                    | 85                                      | 0,52               | 10,5 | 1,0 | 0,48 | 1,6 | 3,3 | 2,3 | 0,45 | Residues        |
| M-2                                    | 101                                     | 1,25               | 6,6  | 1,2 | 0,65 | 2,0 | 1,2 | 2,1 | 0,18 | Residues        |
| M-3                                    | 70                                      | 2,10               | 9,6  | 1,5 | 0,62 | 4,0 | 2,0 | 3,2 | 0,24 | Residues        |
| M-4                                    | 94                                      | 0,93               | 10,4 | 4,0 | 0,53 | 3,5 | 3,1 | 4,1 | -    | Residues        |
| M-5                                    | 101                                     | 0,76               | 4,8  | 1,3 | 0,68 | 1,1 | 3,5 | 2,0 | 0,93 | Residues        |
| M-6                                    | 90                                      | 0,83               | 3,6  | 1,2 | 0,88 | 3,4 | 2,0 | 4,8 | 0,42 | Residues        |
| M-7                                    | 73                                      | 0,65               | 4,9  | 1,4 | 0,88 | 1,6 | 2,4 | 2,0 | 0,25 | Residues        |
| M-8                                    | 86                                      | 1,35               | 9,4  | 1,8 | 0,18 | -   | 1,3 | 4,6 | 0,61 | Residues        |
| M-9                                    | 91                                      | 1,00               | 1,2  | 2,1 | 0,17 | 2,5 | -   | 1,5 | -    | Residues        |
| M-10                                   | 110                                     | 0,94               | 8,0  | 1,9 | 0,55 | 3,4 | 0,2 | 1,2 | 0,36 | Residues        |
| M-11                                   | 75                                      | 1,05               | 6,2  | 1,0 | 0,46 | 0,3 | 3,0 | 2,3 | 0,27 | Residues        |
| M-12                                   | 89                                      | 1,02               | 7,0  | 1,2 | 0,51 | 2,0 | 1,5 | -   | 0,54 | Residues        |
| M-13                                   | 93                                      | 0,50               | 2,1  | 2,4 | 0,42 | 2,1 | 2,1 | 4,2 | 0,30 | Residues        |

Table 2

| Type | Average<br>particle<br>size<br>( $\mu\text{m}$ ) | Composition (wt%) |     |     |                    |
|------|--|-------------------|-----|-----|--------------------|
|      |  | Mo                | Cr  | Si  | Co +<br>impurities |
| A-1  | 76   | 20,5              | 8,4 | 2,3 | Residues           |
| A-2  | 92   | 34,7              | 8,1 | 2,6 | Residues           |
| A-3  | 65   | 28,3              | 7,6 | 3,5 | Residues           |
| A-4  | 74   | 28,4              | 6,3 | 1,3 | Residues           |
| A-5  | 81   | 27,6              | 5,2 | 2,2 | Residu B           |
| A-6  | 100  | 30,5              | 9,7 | 2,3 | Residues           |

Hard particles  
Alloy powder  
After forming

Table 3

| Type   | Average<br>particle<br>size<br>( $\mu\text{m}$ ) | Composition (wt %) |      |      |      |      |      | Cr+<br>impurities |
|--|--|--------------------|------|------|------|------|------|-------------------|
|  |  | C                  | W    | Co   | Fe   | Nb   | Si   |                   |
| <b>Hard Particles B forming Alloy Powder</b> |  |                    |      |      |      |      |      |                   |
| B-1  | 112  | 0,52               | 28,3 | 23,2 | 7,8  | 0,85 | 1,12 | Residu S          |
| B-2  | 76   | 1,79               | 22,0 | 28,4 | 10,0 | 1,14 | 1,65 | Residues          |
| B-3  | 80   | 2,93               | 20,1 | 28,6 | 12,2 | 1,46 | 1,23 | Residu S          |
| B-4  | 103  | 2,15               | 15,5 | 26,8 | 14,6 | 1,72 | 0,84 | Residues          |
| B-5  | 68   | 2,16               | 29,3 | 19,7 | 8,4  | 1,66 | 0,56 | Residues          |
| B-6  | 75   | 2,21               | 25,0 | 15,3 | 8,7  | 1,73 | 1,05 | Residues          |
| B-7  | 62   | 1,89               | 27,2 | 29,6 | 8,8  | 1,14 | 1,73 | Residues          |
| B-8  | 108  | 1,83               | 19,1 | 29,4 | 5,2  | 0,94 | 1,64 | Residu S          |
| B-9  | 71   | 1,15               | 22,3 | 19,1 | 14,6 | 1,26 | 1,61 | Residues          |
| B-10   | 100  | 1,24               | 28,1 | 22,3 | 7,4  | 0,22 | 1,22 | Residues          |
| B-11   | 74   | 2,33               | 29,0 | 20,2 | 7,2  | 1,97 | 1,23 | Residues          |
| B-12   | 73   | 2,52               | 26,4 | 21,1 | 6,8  | 1,78 | 0,24 | Residues          |
| B-13   | 82   | 2,21               | 26,5 | 28,6 | 11,1 | 1,92 | 1,93 | Residu S          |

Table 4

| Type | Combination                     |                                       |                                       |
|------|---------------------------------|---------------------------------------|---------------------------------------|
|      | Base metal forming alloy powder | Hard particles A forming alloy powder | Hard particles B forming alloy powder |
| 1    | M-1                             | A-1                                   | B-1                                   |
| 2    | M-2                             | A-2                                   | B-2                                   |
| 3    | M-3                             | A-3                                   | B-3                                   |
| 4    | M-4                             | A-4                                   | B-4                                   |
| 5    | M-5                             | A-5                                   | B-5                                   |
| 6    | M-6                             | A-6                                   | B-6                                   |
| 7    | M-7                             | A-1                                   | B-3                                   |
| 8    | M-8                             | A-2                                   | B-8                                   |
| 9    | M-9                             | A-3                                   | B-9                                   |
| 10   | M-10                            | A-4                                   | B-10                                  |
| 11   | M-11                            | A-5                                   | B-11                                  |
| 12   | M-12                            | A-6                                   | B-12                                  |
| 13   | M-13                            | A-1                                   | B-13                                  |
| 1    | M-3                             | A-1                                   | B-1                                   |
| 2    | M-6                             | A-2                                   | B-2                                   |
| 3    | M-9                             | A-3                                   | B-3                                   |
| 4    | M-12                            | A-4                                   | B-4                                   |

COMPARATIVE VALVE SEAT OF THE INVENTION

Set

Table 5

| Type | Whole composition (wt %) |       |      |     |     |     |     |      | CaF <sub>2</sub> | Fe +<br>impurities |
|------|--------------------------|-------|------|-----|-----|-----|-----|------|------------------|--------------------|
|      | C                        | Si    | Co   | Cr  | Mo  | W   | Ni  | Nb   |                  |                    |
| 1    | 0,54                     | 0,52  | 11,9 | 3,3 | 3,5 | 3,6 | 1,4 | 0,54 | 1,2              | residues           |
| 2    | 1,20                     | 0,49  | 12,1 | 5,4 | 3,4 | 3,5 | 1,0 | 0,65 | 5,2              | residues           |
| 3    | 1,97                     | 0,53  | 14,5 | 4,7 | 3,8 | 3,6 | 1,2 | 0,62 | 8,6              | residues           |
| 4    | 0,95                     | 0,052 | 11,6 | 5,1 | 4,3 | 4,1 | 1,3 | 0,53 | 13,2             | residues           |
| 5    | 0,90                     | 1,02  | 10,2 | 6,0 | 4,7 | 5,7 | 1,0 | 0,71 | 7,5              | residues           |
| 6    | 0,81                     | 0,60  | 8,3  | 5,7 | 4,2 | 5,2 | 1,3 | 0,83 | 8,81             | residues           |
| 7    | 0,78                     | 0,72  | 15,7 | 5,9 | 4,6 | 5,5 | 1,1 | 0,81 | 11,2             | residues           |
| 8    | 1,31                     | 0,81  | 12,6 | 2,3 | 3,4 | 4,7 | 1,5 | 0,22 | 14,7             | residues           |
| 9    | 0,85                     | 0,65  | 11,6 | 7,8 | 3,3 | 4,3 | 1,6 | 0,31 | 10,2             | residues           |

VALVE SEAT OF THE  
INVENTION

Table 6

| Type | C     | Si   | Co   | Cr  | Mo   | W    | Ni  | Nb   | CaF <sub>2</sub> | Fe + impurities | Whole composition (wt %) |    |
|------|-------|------|------|-----|------|------|-----|------|------------------|-----------------|--------------------------|----|
|      |       |      |      |     |      |      |     |      |                  |                 | the invention            |    |
| 10   | 0,90  | 0,53 | 12,4 | 7,6 | 1,51 | 4,0  | 1,3 | 0,52 | 9,2              | Residues        | 10                       | 10 |
| 11   | 0,96  | 0,58 | 14,5 | 3,1 | 6,0  | 3,6  | 0,8 | 0,49 | 13,7             | Residues        | 11                       | 11 |
| 12   | 1,01  | 0,72 | 11,7 | 5,2 | 3,9  | 1,52 | 0,9 | 0,50 | 4,2              | Residues        | 12                       | 12 |
| 13   | 0,61  | 0,63 | 12,1 | 4,5 | 3,9  | 5,7  | 1,9 | 0,52 | 2,1              | Residues        | 13                       | 13 |
| 1    | 2,14* | 0,26 | 11,2 | 4,5 | 2,2  | 3,6  | 1,1 | 0,61 | 10,6             | Residues        | 1                        | 14 |
| 2    | 0,62  | 0,71 | 10,5 | 4,2 | 6,2* | 3,8  | 1,0 | 0,56 | 6,8              | Residues        | 2                        | 15 |
| 3    | 0,93  | 0,33 | 6,8* | 3,5 | 2,2  | 1,8  | 1,6 | 0,21 | 17,2             | Residues        | 3                        | 16 |
| 4    | 0,91  | 0,52 | 8,0  | 2,6 | 2,0  | 0,3* | 0,9 | 0,43 | 0,8*             | Residues        | 4                        | 17 |

( \* indicates component outside the range of the invention)

Table 7

| Type | Hard particles (area %) |    | CaF <sub>2</sub><br>particles<br>(area %) | Porosity<br>(%) | Maximum<br>worn depth<br>depth(μm) | Maximum<br>worn depth<br>of valve<br>(μm) |
|------|-------------------------|----|---|-----------------|------------------------------------|---|
|      | A                       | B  |   |                 |                                    |   |
| 1    | 25                      | 75 | 6,1                                       | 3,1             | 23,8                               | 101                                       |
| 2    | 51                      | 49 | 14,5                                      | 15,1            | 19,7                               | 41  |
| 3    | 73                      | 27 | 10,2                                      | 25,7            | 17,9                               | 56  |
| 4    | 27                      | 73 | 6,4                                       | 39,0            | 5,2                                | 4   |
| 5    | 31                      | 69 | 17,5                                      | 22,6            | 16,0                               | 16  |
| 6    | 60                      | 40 | 12,2                                      | 26,7            | 9,7                                | 45  |
| 7    | 49                      | 51 | 24,2                                      | 33,3            | 9,0                                | 15  |
| 8    | 64                      | 36 | 9,7                                       | 44,5            | 21,6                               | 64  |
| 9    | 52                      | 48 | 25,5                                      | 30,3            | 21,3                               | 26  |
|      |                         |    |   |                 | 30                                 |   |

Valve seat of the invention

Table 8

| Type | Hard particles (area %) |     | CaF <sub>2</sub><br>particles<br>(area %) | Porosity<br>(%) | Maximum<br>worn depth<br>(μm) | Maximum<br>worn depth<br>of valve<br>(μm) |
|------|-------------------------|-----|---|-----------------|-------------------------------|---|
|      | A                       | B   |   |                 |                               |   |
| 1    | 10                      | 30  | 70  | 15,2            | 27,3                          | 57  |
| 11   | 66                      | 34  | 17,1                                      | 42,3            | 21,2                          | 16  |
| 12   | 61                      | 39  | 15,4                                      | 12,3            | 18,4                          | 22  |
| 13   | 52                      | 48  | 17,5                                      | 6,1             | 14,6                          | 14  |
| 1    | 49                      | 51  | 3,2*                                      | 31,7            | 7,0                           | 345                                       |
| 2    | 45                      | 55  | 28,6*                                     | 21,5            | 24,3                          | 279                                       |
| 3    | 83*                     | 17* | 9,8                                       | 51,0*           | 18,9                          | 215                                       |
| 4    | 16*                     | 4   | 84*                                       | 20,1            | 2,5*                          | 145                                       |
|      |                         |     |   |                 | 16,8                          | 250                                       |
|      |                         |     |   |                 | 112                           |   |

(\* indicates component outside the range of the invention)

Table 9

| Type                        | Symbol of main body | Copper or copper alloy infiltrating material | Maximum worn depth ( $\mu\text{m}$ ) | Maximum worn depth of valve ( $\mu\text{m}$ ) |
|-----------------------------|---------------------|--|--------------------------------------|---|
| VALVE SEAT OF THE INVENTION | 1                   | Pure copper                                  | 63                                   | 18  |
|                             | 2                   | Pure copper                                  | 36                                   | 15  |
|                             | 3                   | Pure copper                                  | 39                                   | 7   |
|                             | 4                   | Cu alloy 1                                   | 42                                   | 15  |
|                             | 5                   | Cu alloy 2                                   | 27                                   | 17  |
|                             | 6                   | Cu alloy 2                                   | 26                                   | 9   |
|                             | 7                   | Cu alloy 3                                   | 13                                   | 8   |
|                             | 8                   | Cu alloy 1                                   | 46                                   | 11  |
|                             | 9                   | Cu alloy 2                                   | 19                                   | 16  |
|                             | 10                  | Cu alloy 3                                   | 31                                   | 19  |
|                             | 11                  | Cu alloy 2                                   | 12                                   | 25  |
|                             | 12                  | Pure copper                                  | 15                                   | 8   |
|                             | 13                  | Pure copper                                  | 8                                    | 26  |
| COMPARATIVE VALVE SEAT      | 1                   | Pure copper                                  | 210                                  | 142   |
|                             | 2                   | Cu alloy 1                                   | 148                                  | 104   |
|                             | 3                   | Cu alloy 2                                   | 183                                  | 115   |
|                             | 4                   | Cu alloy 3                                   | 215                                  | 123   |

Table 10

| Type | Symbol of main body | Lead or lead alloy infiltrating material | Maximum worn depth ( $\mu\text{m}$ ) | Maximum worn depth of valve ( $\mu\text{m}$ ) | VALVE SEAT OF THE INVENTION |    |    |    |    |    |    |    |    |    |    |    |    |
|------|---------------------|--|--------------------------------------|---|-----------------------------|----|----|----|----|----|----|----|----|----|----|----|----|
|      |                     |  |                                      |   | VALVE SEAT OF THE INVENTION |    |    |    |    |    |    |    |    |    |    |    |    |
| 1    | 1                   | Pure lead                                | 88                                   | 9   | 1                           | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  |
| 2    | 2                   | Pure lead                                | 60                                   | 8   | 2                           | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  |
| 3    | 3                   | Pure lead                                | 62                                   | 7   | 3                           | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3  |
| 4    | 4                   | Alloy a                                  | 67                                   | 8   | 4                           | 4  | 4  | 4  | 4  | 4  | 4  | 4  | 4  | 4  | 4  | 4  | 4  |
| 5    | 5                   | Alloy a                                  | 25                                   | 11  | 5                           | 5  | 5  | 5  | 5  | 5  | 5  | 5  | 5  | 5  | 5  | 5  | 5  |
| 6    | 6                   | Alloy b                                  | 28                                   | 17  | 6                           | 6  | 6  | 6  | 6  | 6  | 6  | 6  | 6  | 6  | 6  | 6  | 6  |
| 7    | 7                   | Alloy a                                  | 29                                   | 8   | 7                           | 7  | 7  | 7  | 7  | 7  | 7  | 7  | 7  | 7  | 7  | 7  | 7  |
| 8    | 8                   | Alloy b                                  | 41                                   | 12  | 8                           | 8  | 8  | 8  | 8  | 8  | 8  | 8  | 8  | 8  | 8  | 8  | 8  |
| 9    | 9                   | Alloy b                                  | 16                                   | 18  | 9                           | 9  | 9  | 9  | 9  | 9  | 9  | 9  | 9  | 9  | 9  | 9  | 9  |
| 10   | 10                  | Pure lead                                | 15                                   | 6   | 10                          | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| 11   | 11                  | Pure lead                                | 17                                   | 9   | 11                          | 11 | 11 | 11 | 11 | 11 | 11 | 11 | 11 | 11 | 11 | 11 | 11 |
| 12   | 12                  | Pure lead                                | 24                                   | 7   | 12                          | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 |
| 13   | 13                  | Pure lead                                | 19                                   | 11  | 13                          | 13 | 13 | 13 | 13 | 13 | 13 | 13 | 13 | 13 | 13 | 13 | 13 |
| 14   | 1                   | Pure lead                                | 326                                  | 145   | 1                           | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  | 1  |
| 15   | 2                   | Pure lead                                | 360                                  | 115   | 2                           | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  |
| 16   | 3                   | Alloy a                                  | 145                                  | 73  | 3                           | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3  | 3  |
| 17   | 4                   | Alloy b                                  | 137                                  | 81  | 4                           | 4  | 4  | 4  | 4  | 4  | 4  | 4  | 4  | 4  | 4  | 4  | 4  |

## Industrial Applicability

[0028] It is apparent from the results shown in Table 4 to Table 10 that any of the valve seats 1 - 13 of the present invention, the copper-infiltrated valve seats 1 - 13 of the present invention, and the lead-infiltrated valve seats 1 - 13 of the present invention exhibits excellent wear resistance with a low counterpart attacking property under a high temperature operating condition; whereas, when the ratio of the hard particles of the Fe-based sintered alloy which constitutes

the valve seats and further the ratios of the hard particles and CaF<sub>2</sub> fall outside the range of the present invention as found in the comparative valve seats 1 - 4, the comparative copper-infiltrated comparative valve seats 1 - 4, and the comparative lead-infiltrated comparative valve seats 1 - 4, the wear resistance is lowered and the counterpart attacking property is increased.

5 [0029] As described above, in the valve seat of the present invention, the high temperature and ordinary temperature wear resistance is greatly improved particularly by the hard particles A and B in the Fe-based sintered alloy which constitutes the valve seat. Further, the wear resistance at the initial operation of an internal combustion engine and when the internal combustion engine is in operation at a low speed is improved by the hard particles B and the CaF<sub>2</sub> which are contained in the Fe-based sintered alloy in a coexisted state. Accordingly, the valve seat of the present invention  
10 exhibits excellent wear resistance not only when the internal combustion engine is operated at an ordinary temperature but also when it is operated at a high temperature.

### Claims

15 1. A valve seat excellent in wear resistance made of Fe-based sintered alloy, the Fe-based sintered alloy comprising, as a whole composition, by weight

C: 0. 5 - 2 %, Si: 0.05 - 1 %,  
Co: 8 - 16 %, Cr: 2 - 8 %,  
20 Mo: 1.5 - 6 %, W: 1.5 - 6 %,  
Ni: 0.5 - 2 %, Nb: 0.05 - 1 %, and  
calcium fluoride: 1 - 15 %,

25 with a balance of Fe and inevitable impurities, wherein the Fe-based sintered alloy has such a structure that Co-based alloy hard particles A, which comprise Co-Mo-Cr alloy and have high temperature wear resistance, and Cr-based alloy hard particles B, which comprise Cr-W-Co-Fe alloy and have ordinary temperature wear resistance, are dispersed and distributed in an alloy steel base at a ratio of 6 - 26 area % in a total amount when they are observed on a structure photograph recorded by an optical microscope as well as the ratio of the hard particles A to the hard particles is 25 - 75 area % and further calcium fluoride particles are dispersed and distributed in the alloy steel base  
30 at a ratio of 3 - 45 area ratio likewise, and the Fe-based sintered alloy has a porosity of 5 - 25 %.

2. A valve seat excellent in wear resistance made of Fe-based sintered alloy, the Fe-based sintered alloy comprising, as a whole composition, by weight

35 C: 0. 5 - 2 %, Si: 0.05 - 1 %,  
Co: 8 - 16 %, Cr: 2 - 8 %,  
Mo: 1.5 - 6 %, W: 1.5 - 6 %,  
Ni: 0.5 - 2 %, Nb: 0.05 - 1 %, and  
calcium fluoride: 1 - 15 %,

40 with a balance of Fe and inevitable impurities, wherein the Fe-based sintered alloy has such a structure that Co-based alloy hard particles A, which comprise Co-Mo-Cr alloy and have high temperature wear resistance, and Cr-based alloy hard particles B, which comprise Cr-W-Co-Fe alloy and have ordinary temperature wear resistance, are dispersed and distributed in an alloy steel base at a ratio of 6 - 26 area % in a total amount when they are observed on a structure photograph recorded by an optical microscope as well as the ratio of the hard particles A to the hard particles is 25 - 75 area % and further calcium fluoride particles are dispersed and distributed in the alloy steel base  
45 at a ratio of 3 - 45 area ratio likewise, and the Fe-based sintered alloy has a porosity of 5 - 25 %, and copper or copper alloy, or lead or lead alloy is infiltrated into the Fe-based sintered alloy.

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP98/05095

## A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl<sup>6</sup> C22C38/00, 304, C22C38/52, C22C33/02, C23C10/22, C23C10/26, F01L3/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl<sup>6</sup> C22C38/00-38/60, C22C33/02, C23C10/00-10/60, F01L3/02Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-1999  
Kokai Jitsuyo Shinan Koho 1971-1999 Jitsuyo Shinan Toroku Koho 1996-1999

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                           | Relevant to claim No. |
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| Y         | JP, 3-158445, A (Mitsubishi Materials Corp.), 8 July, 1991 (08. 07. 91)<br>& DE, 4036614, A & US, 5031878, A | 1, 2                  |
| Y         | JP, 8-311624, A (Sumitomo Electric Industries, Ltd.), 26 November, 1996 (26. 11. 96) (Family: none)          | 1, 2                  |
| Y         | JP, 6-299284, A (Fuji Oozx Inc.), 25 October, 1994 (25. 10. 94) (Family: none)                               | 1, 2                  |
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| A         | JP, 3-158444, A (Mitsubishi Materials Corp.), 8 July, 1991 (08. 07. 91) (Family: none)                       | 1, 2                  |

 Further documents are listed in the continuation of Box C.  See patent family annex.

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| Date of the actual completion of the international search<br>2 March, 1999 (02. 03. 99) | Date of mailing of the international search report<br>9 March, 1999 (09. 03. 99) |
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**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/JP98/05095

C.(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages     | Relevant to claim No. |
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Form PCT/ISA/210 (continuation of second sheet) (July 1992)